A Tale of Two Extremes: Contrasting NH_3 at the Bakersfield and Pasadena Supersites

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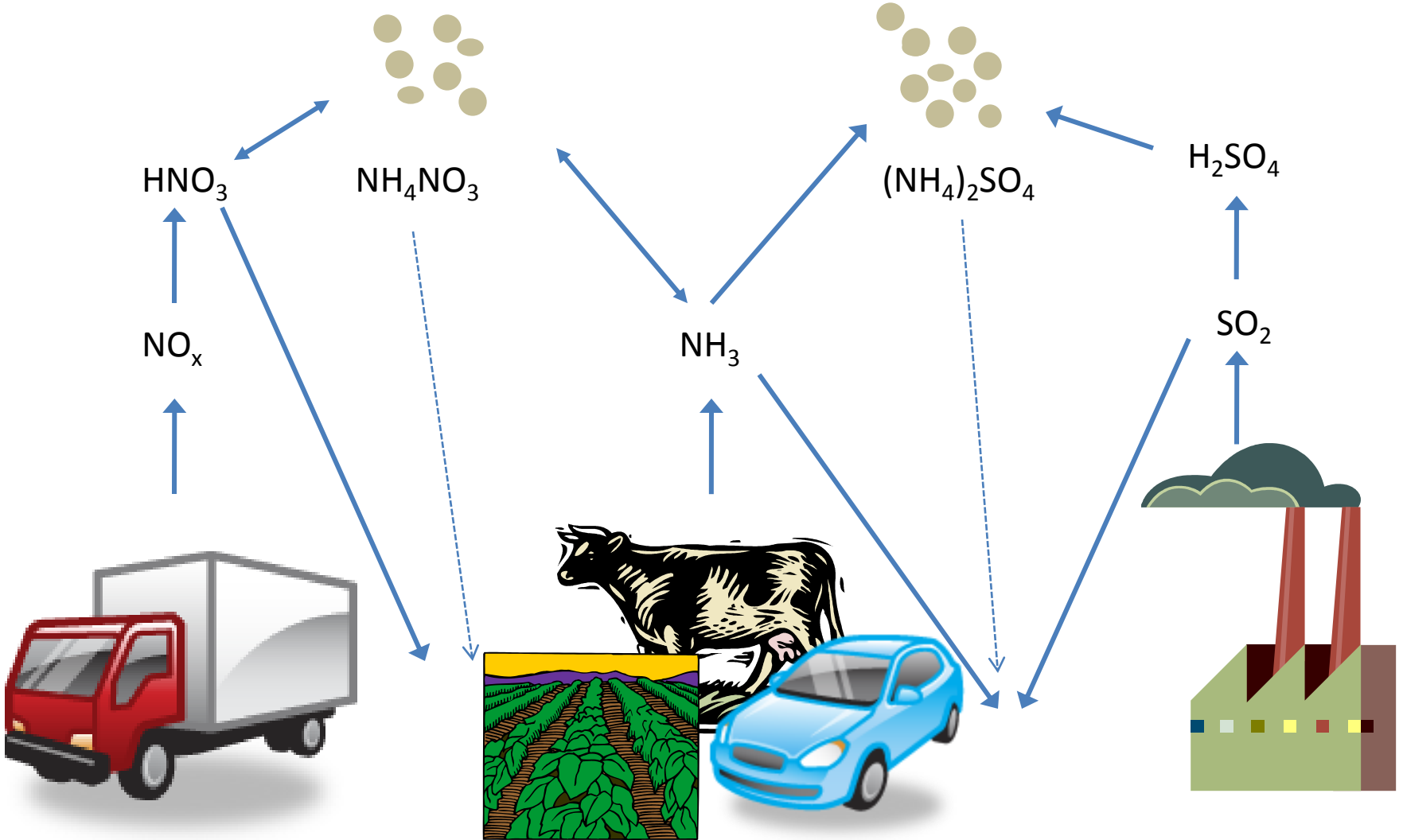
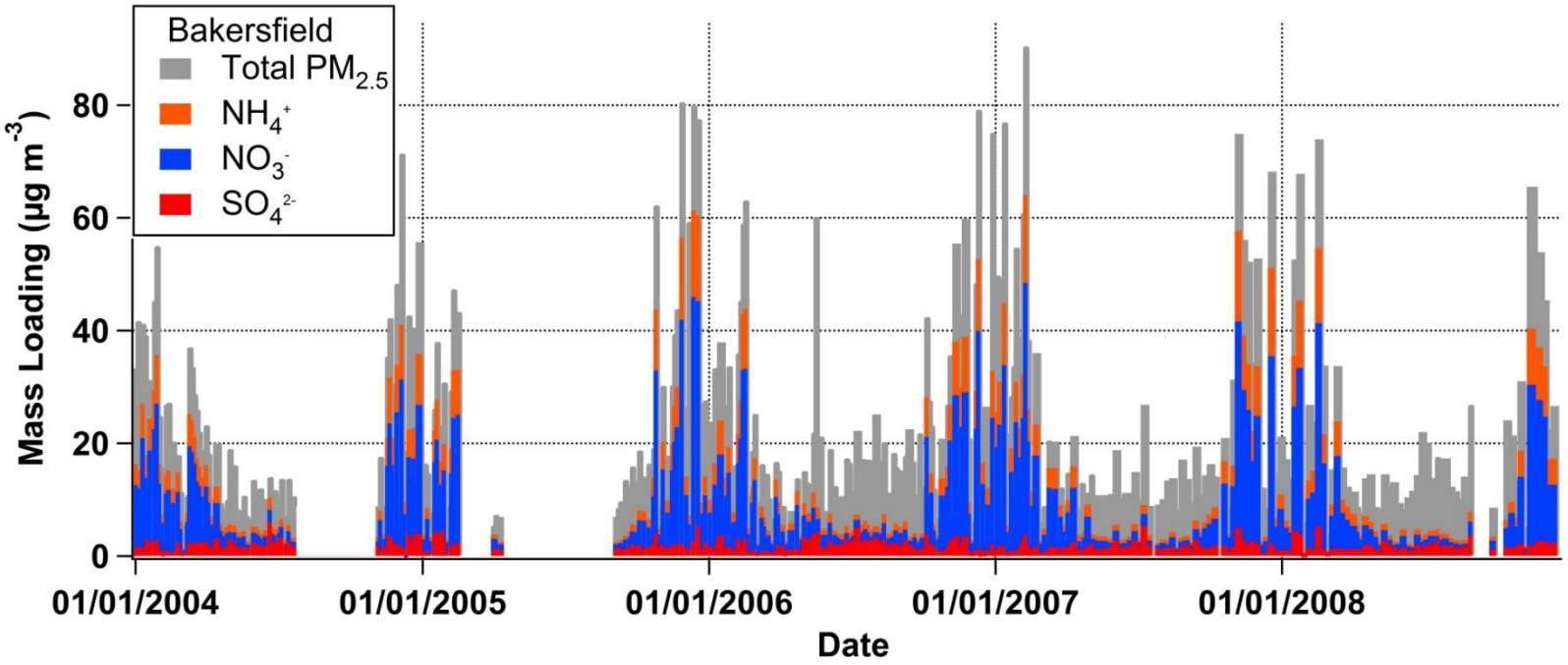
Ammonia and Particle Formation

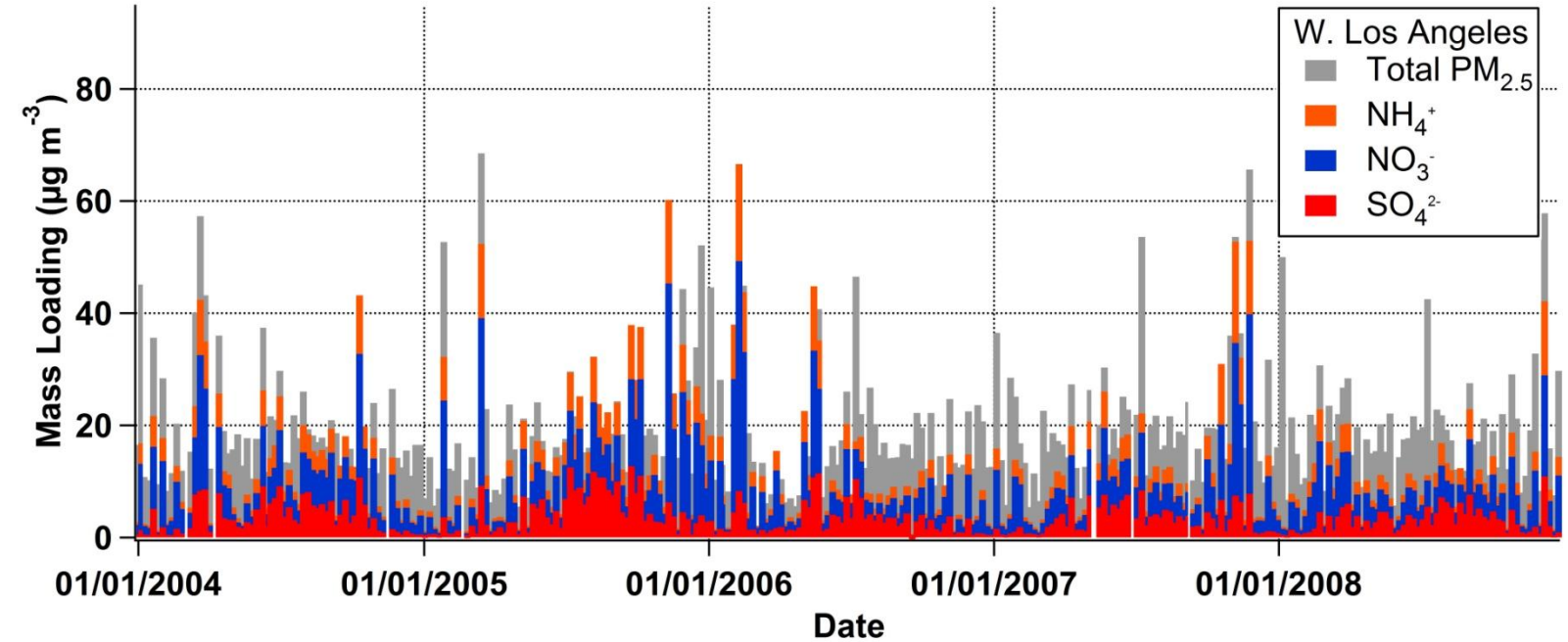
Highly coupled and non-linear



Historical CARB data

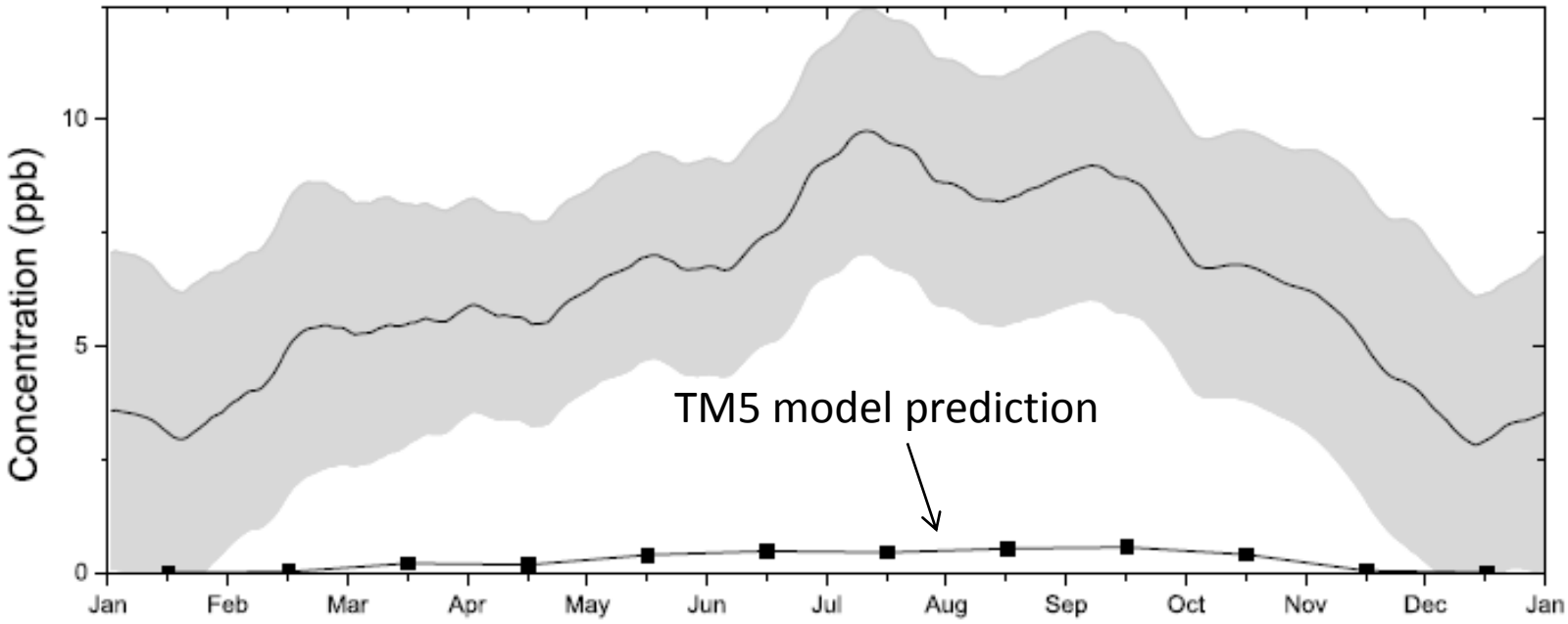


seasonality in NH_4NO_3



seasonality in $(NH_4)_2SO_4$

NH_3 in the San Joaquin Valley



(a) NH_3 concentration at 700m (IASI morning orbit)

Clarisse et al., *JGR*, 2010

Mobile Emissions of NH_3

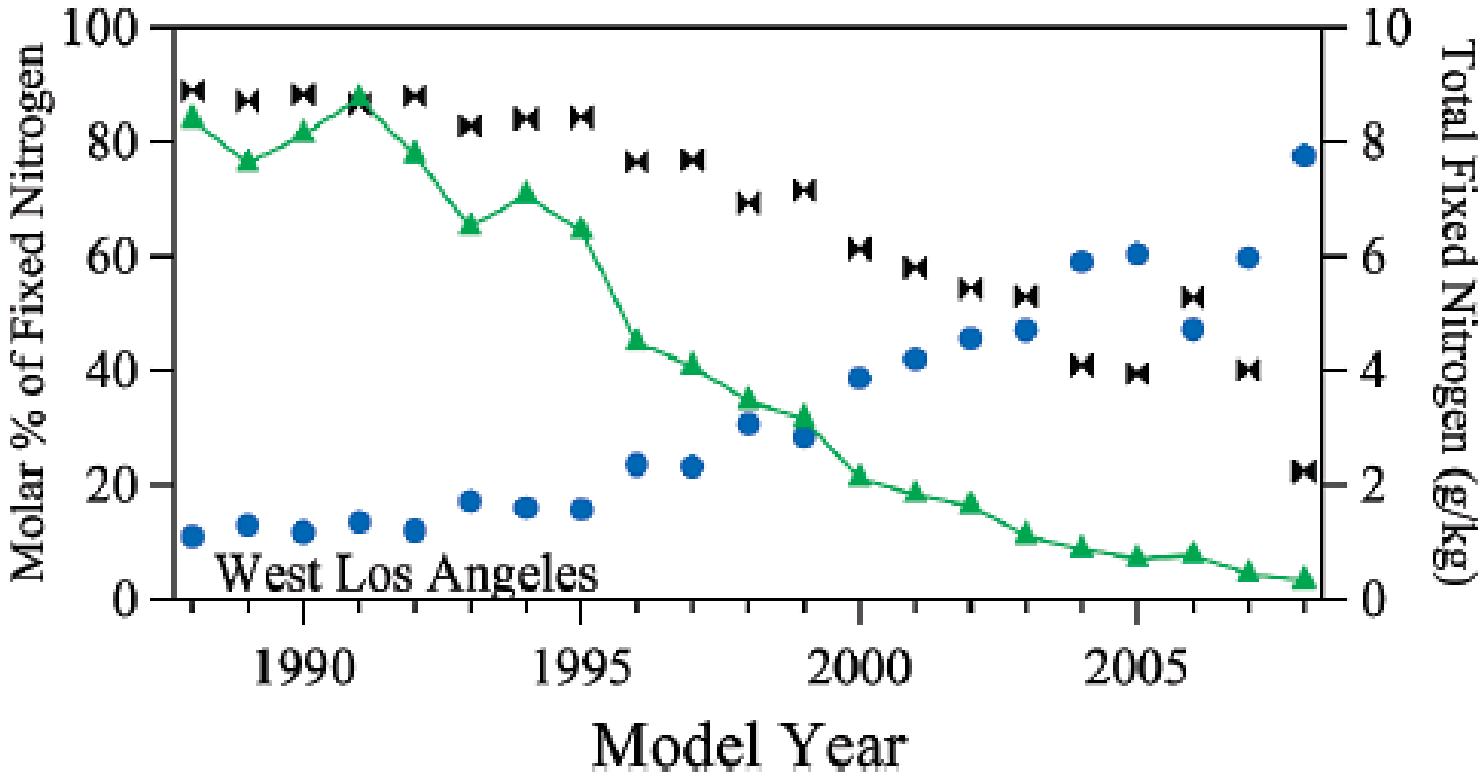
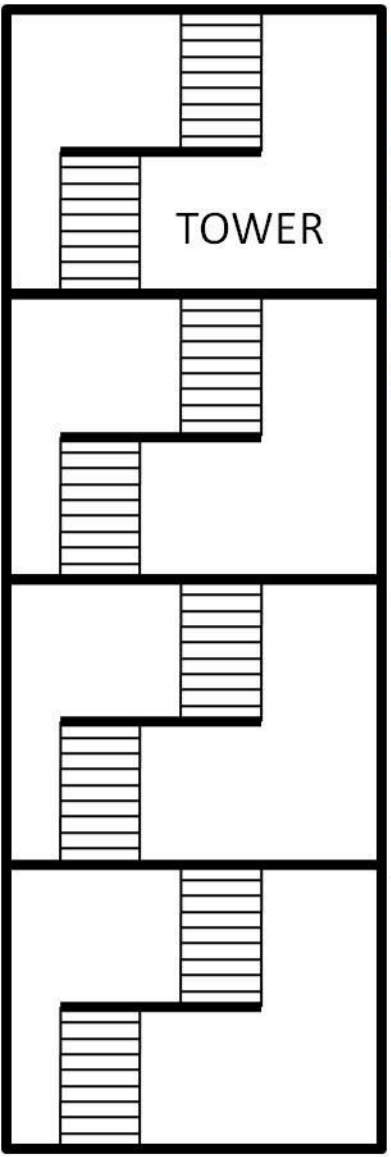


FIGURE 5. Total fixed nitrogen in g/kg (line and triangles, right axis) with the molar percent composition distributed between the NO_x (bowties, left axis) component and the NH_3 component (circles, left axis).

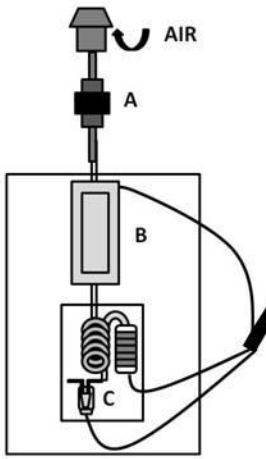
Mobile emissions of NH_3 comparable to NO_x in new, aggressively driven, vehicles

Bishop et al., *ES&T*, 2010

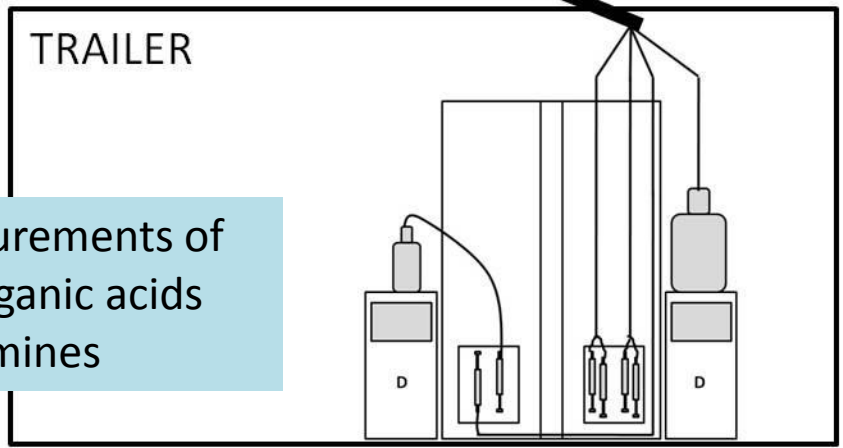
AIM-IC in Bakersfield



A – $PM_{2.5}$ impactor
B – membrane denuder
C – particle collection chamber
D – ion chromatographs

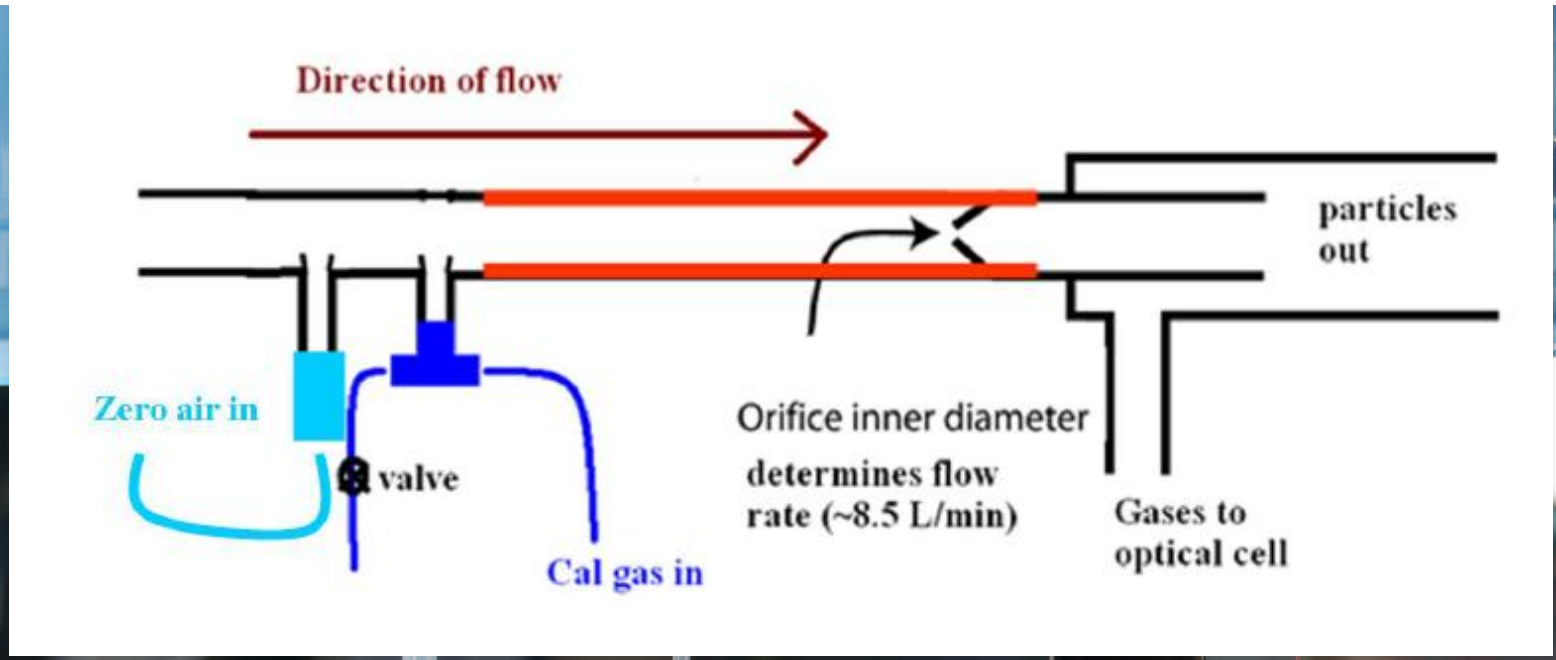


~ 20 m



Hourly gas and $PM_{2.5}$ measurements of
SO_4^{2-}, NO_3^-, Cl^-, Br^-, NO_2^-, organic acids
NH_4^+, K^+, Na^+, Mg^{2+}, Ca^{2+}, amines

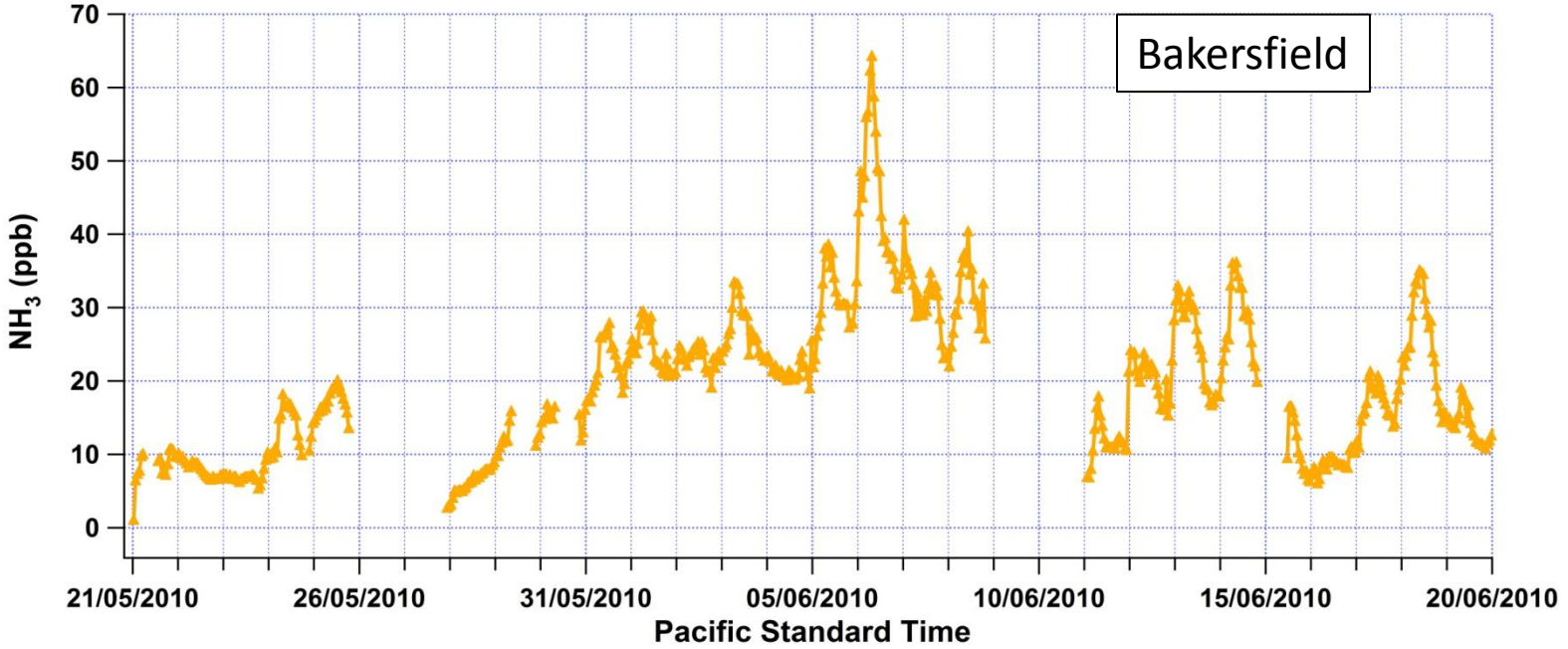
QC-TILDAS in Pasadena

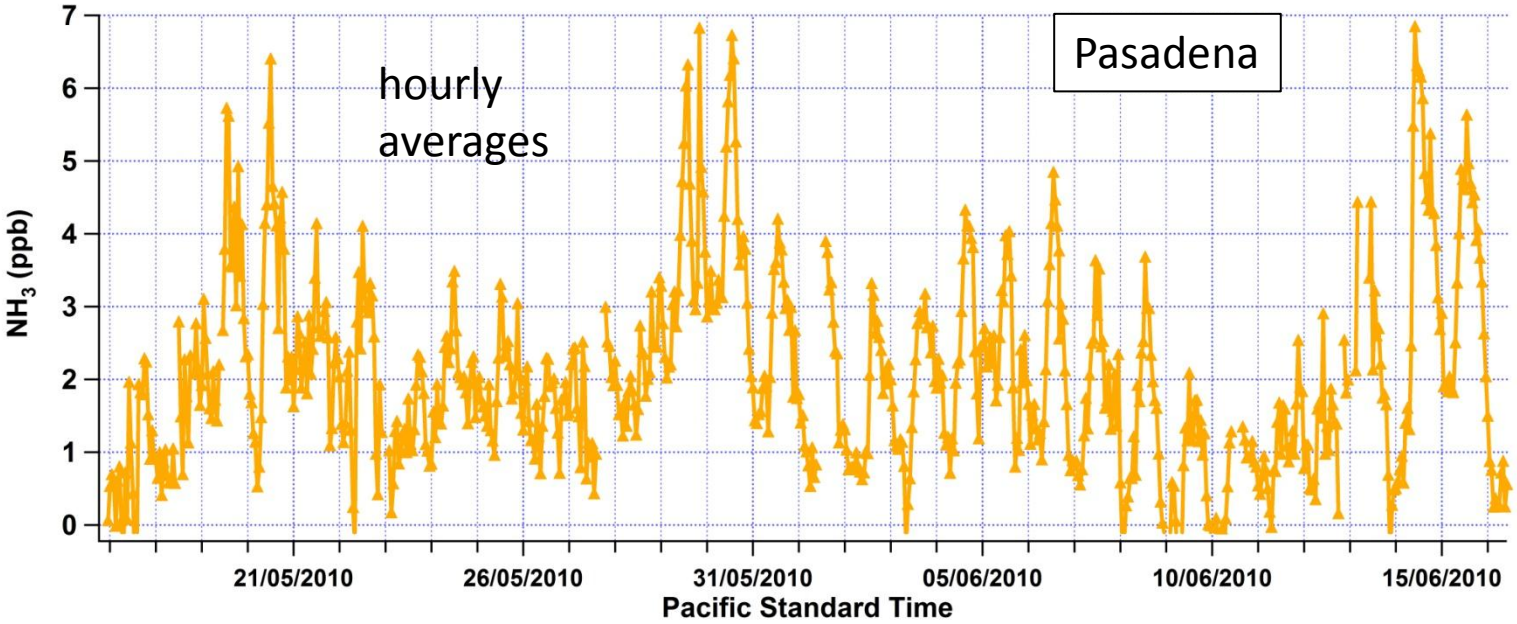


Fast (1Hz) measurements of gas phase NH_3 with minimal sampling artefacts

Ellis et al., *Atmos Meas Tech*, 2010

Ammonia Time Series

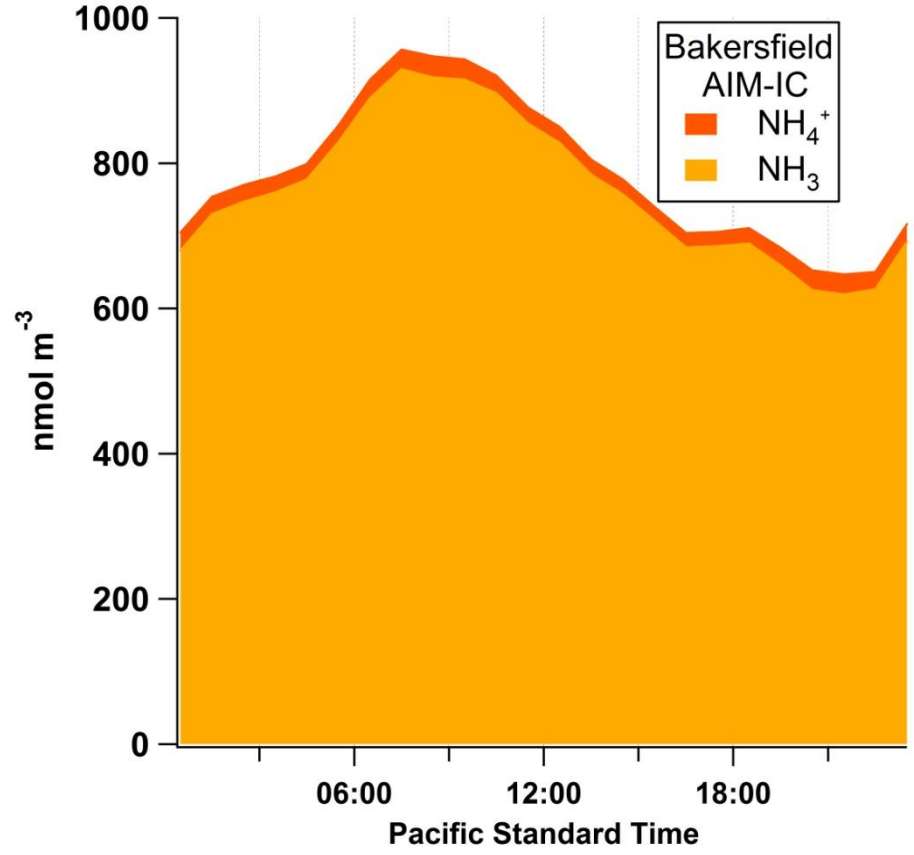


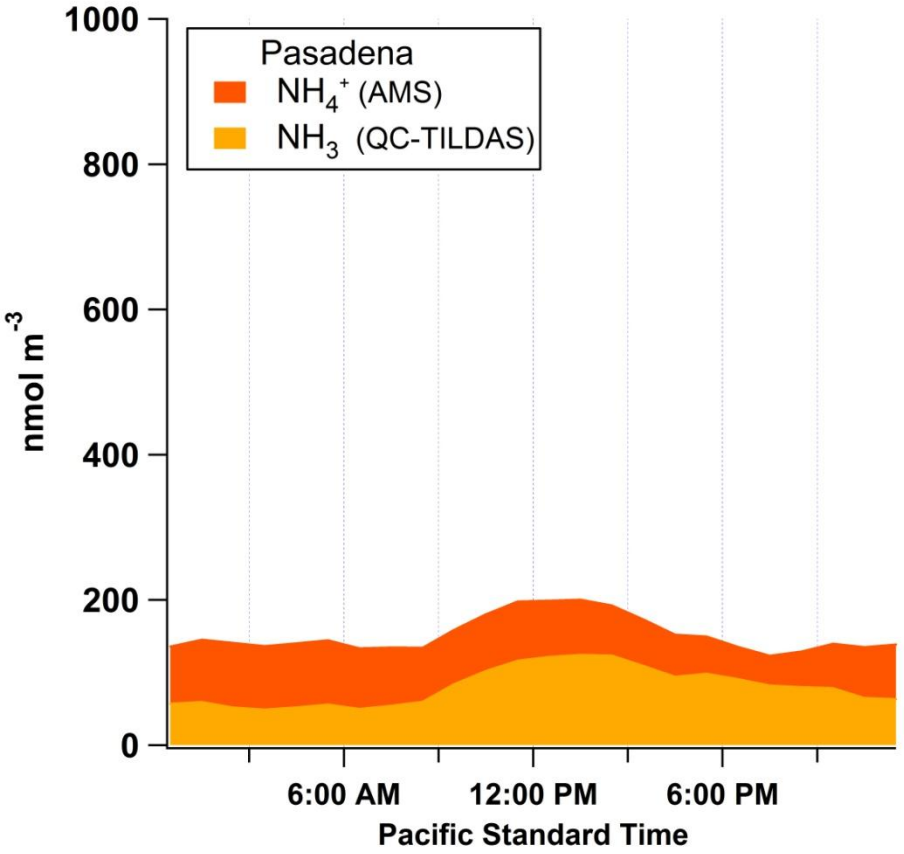


Diurnal Profiles of NH_x Partitioning

Ammonia is controlled by emissions and dilution

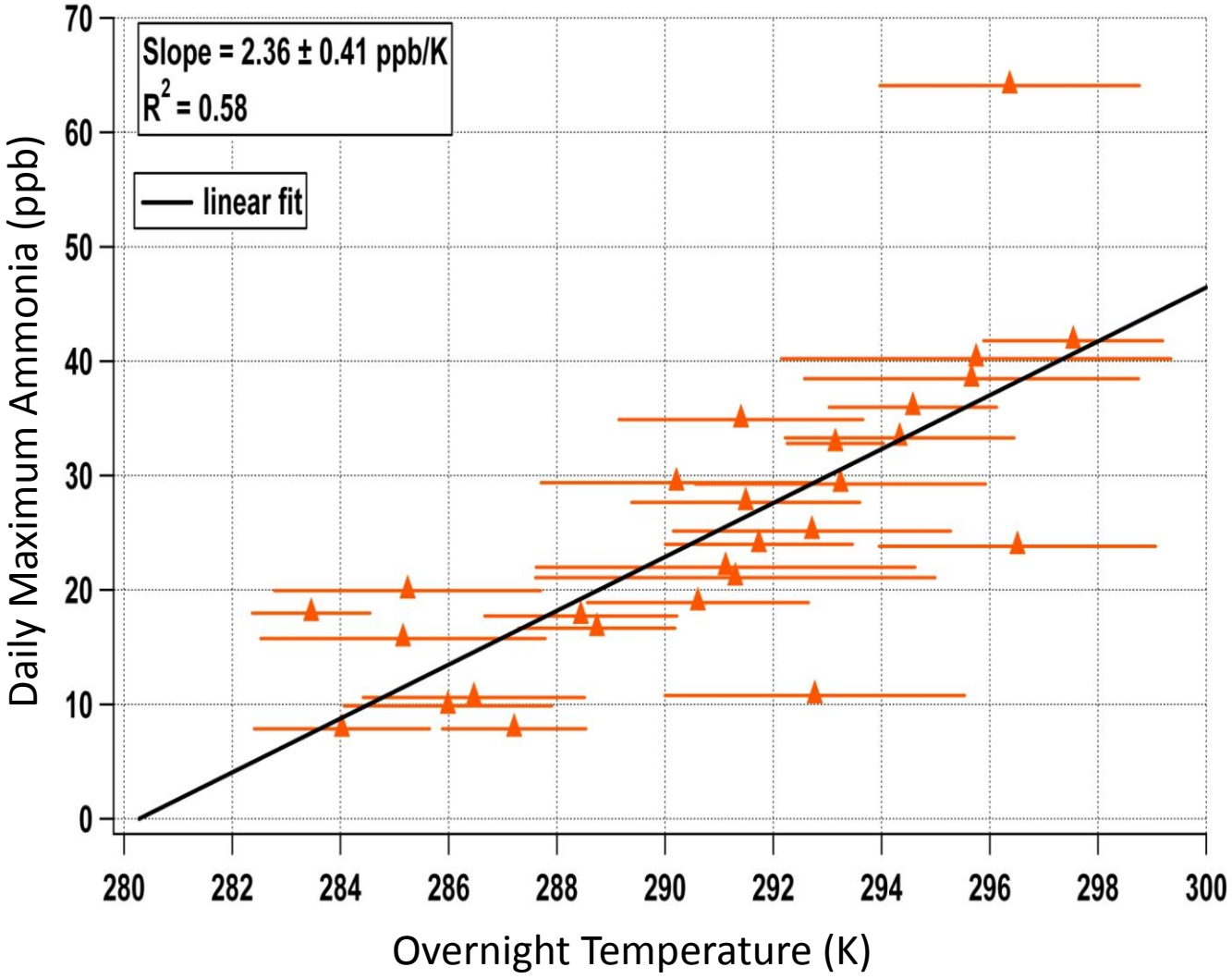
Ammonia is controlled by partitioning and transport



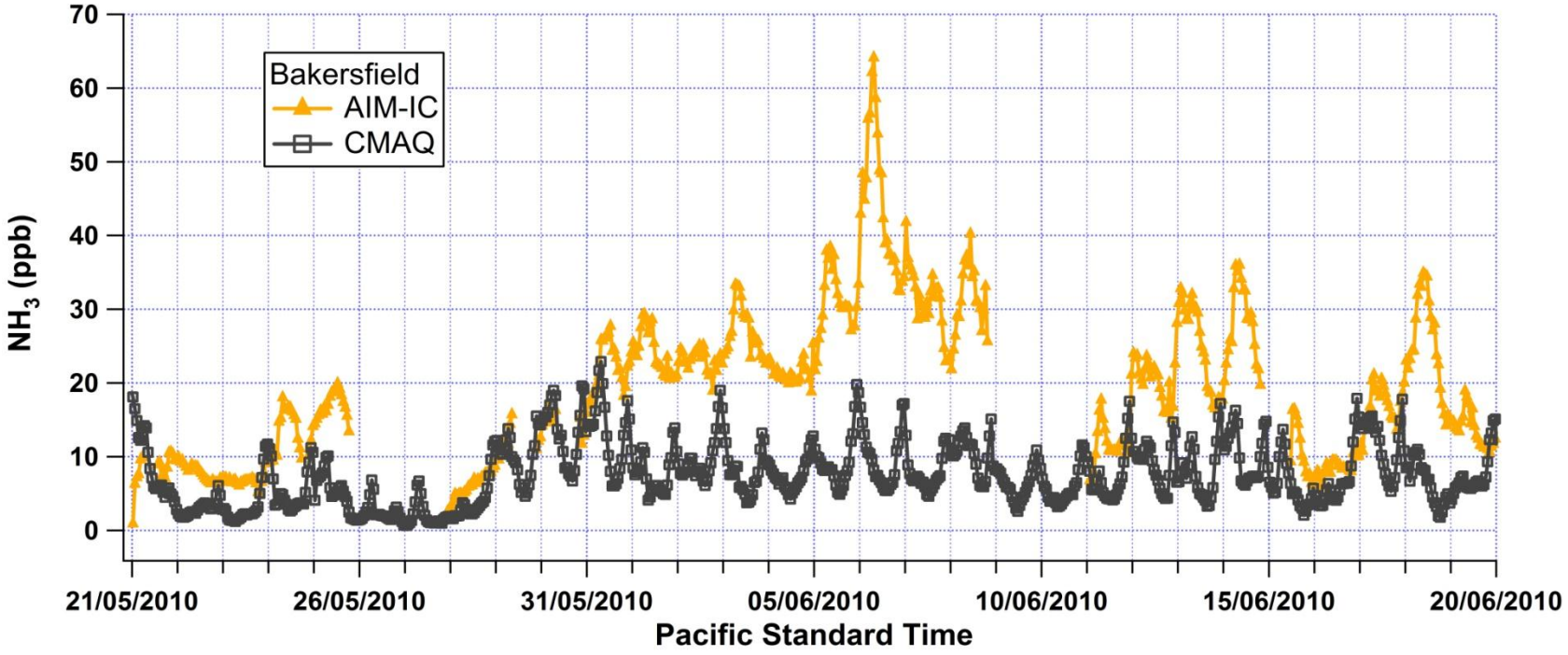


AMS data from Jimenez group, CU

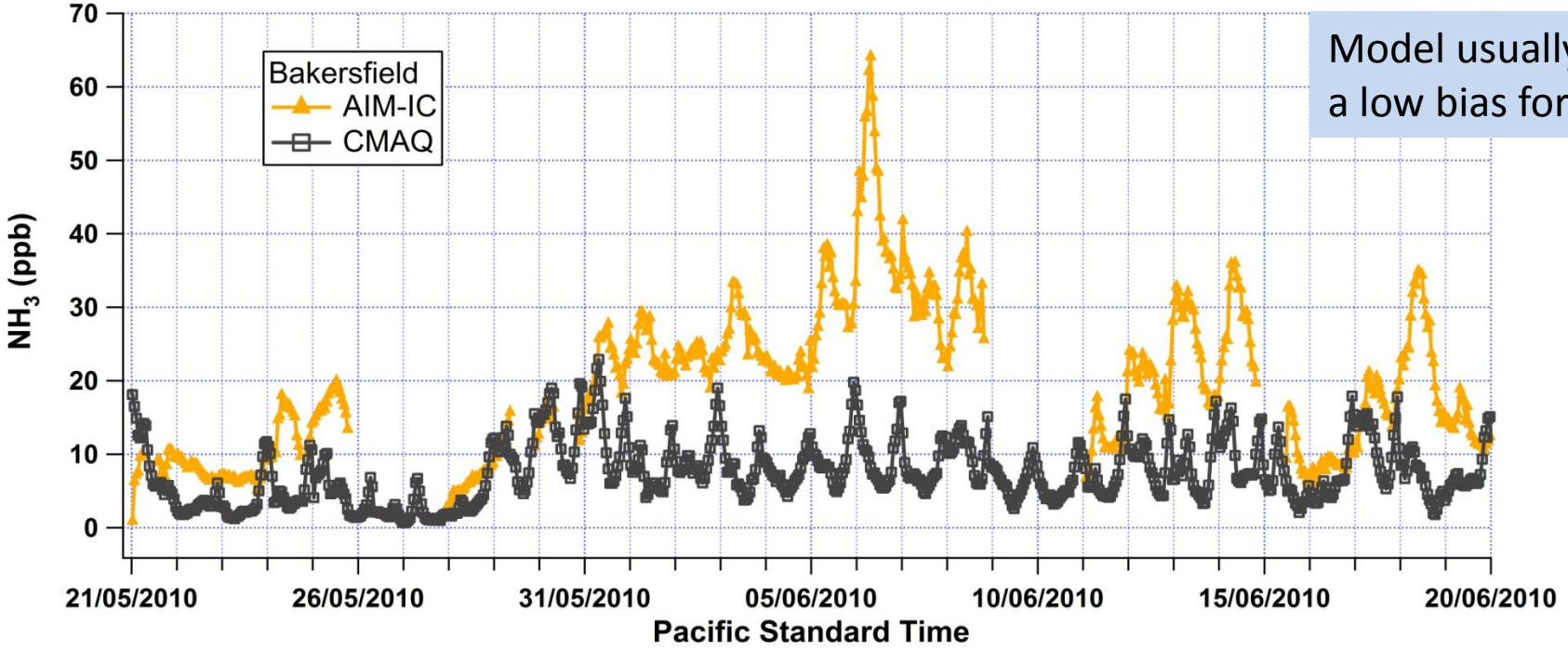
Temperature and NH_3 at Bakersfield



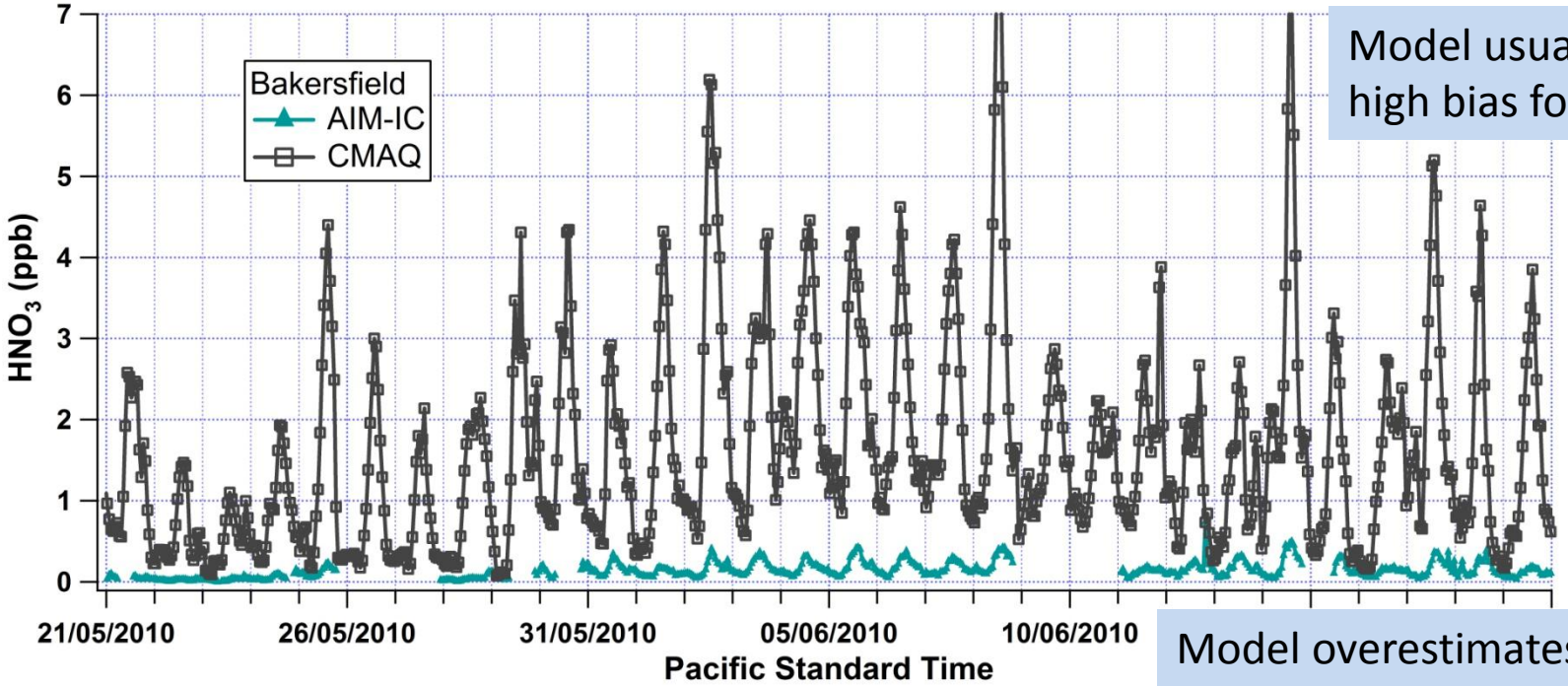
Comparison with Model



CMAQ data courtesy of Kirk Baker, US EPA



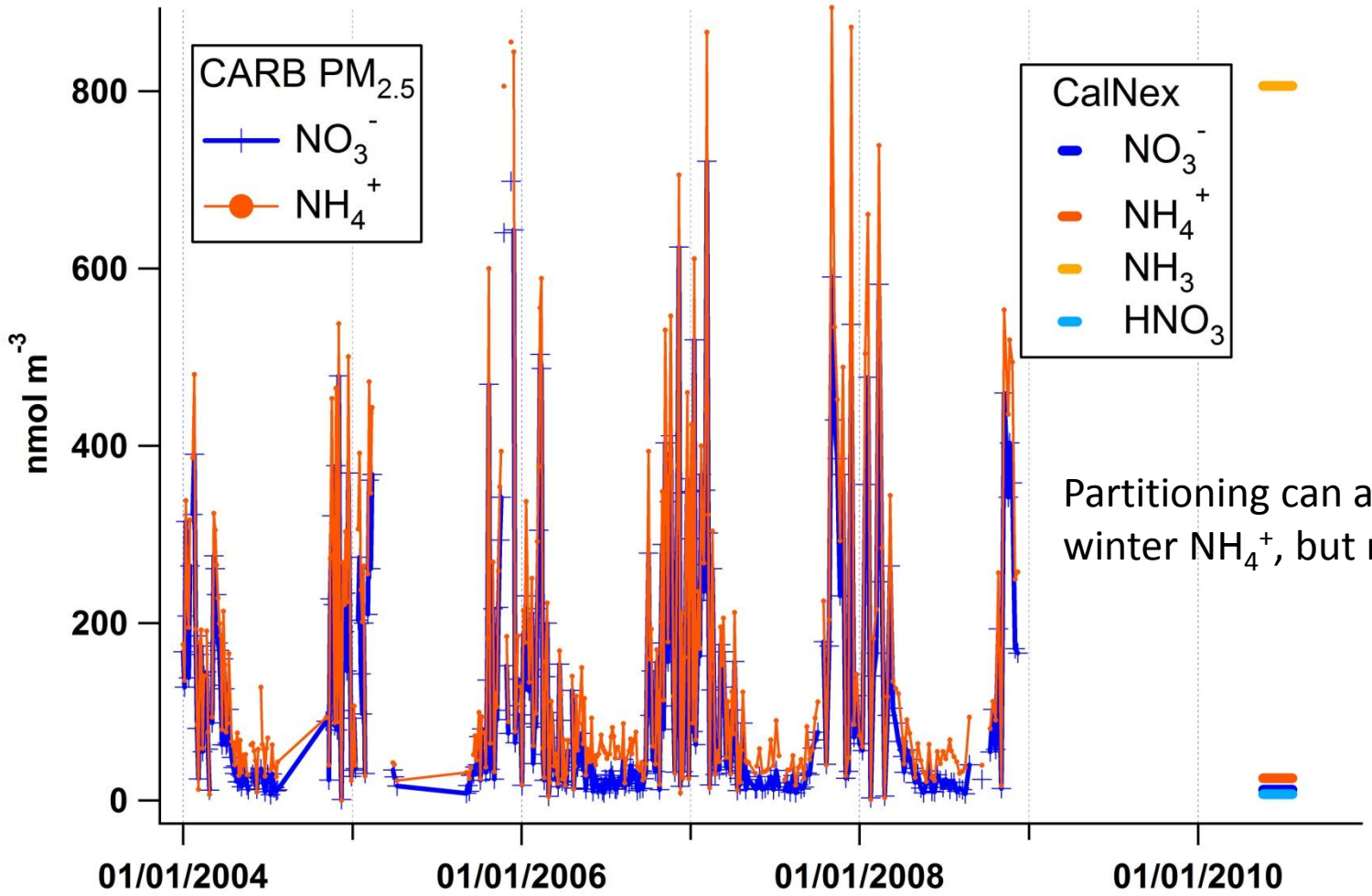
Model usually has a low bias for NH_3



Model usually has a high bias for HNO_3

Model overestimates NH_4NO_3

Historical Record at Bakersfield



Partitioning can account for winter NH_4^+, but not NO_3^-

Summary

- NH_x is ~4 times larger at Bakersfield than at Pasadena
- different processes control NH_3 at the two ground sites
- CMAQ does not represent Bakersfield NH_3 well (emissions or partitioning)

Additional Questions

- aerosol pH
- influence of/on organic acids
- relative contributions of NH_3 emissions sources

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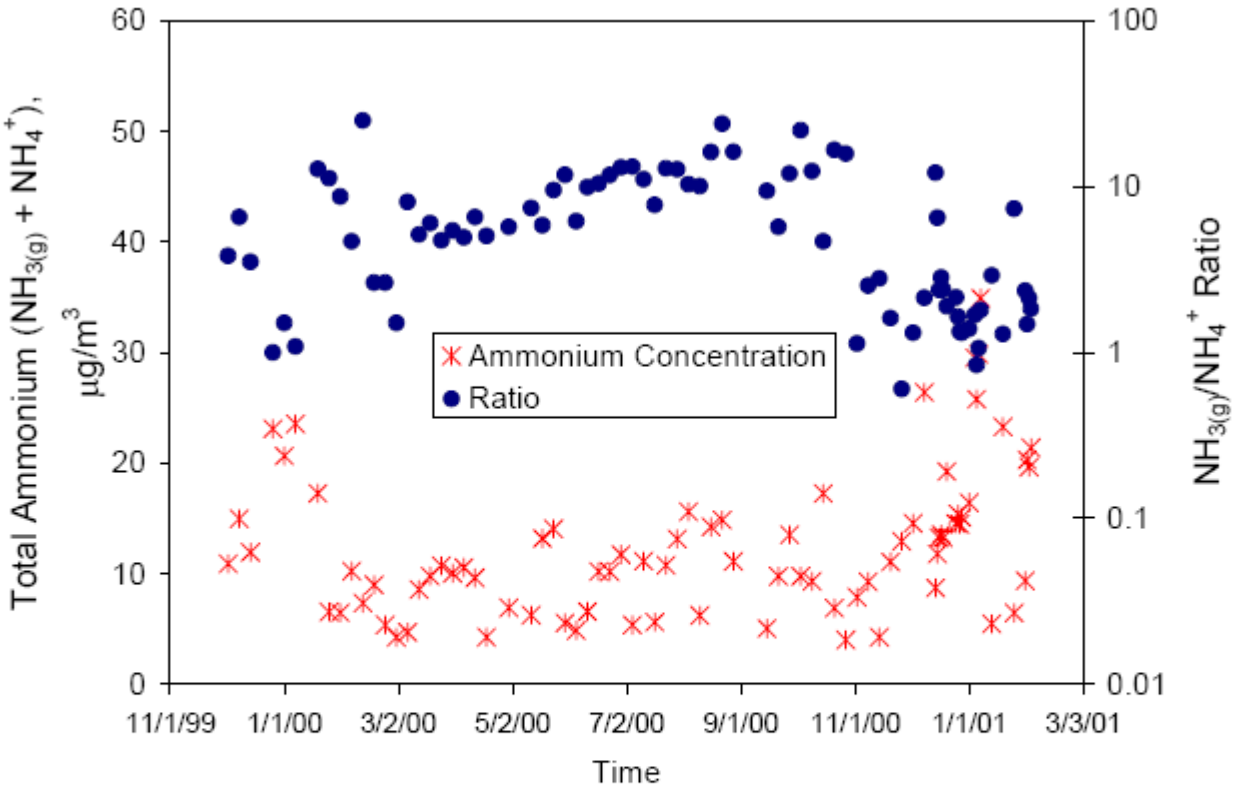
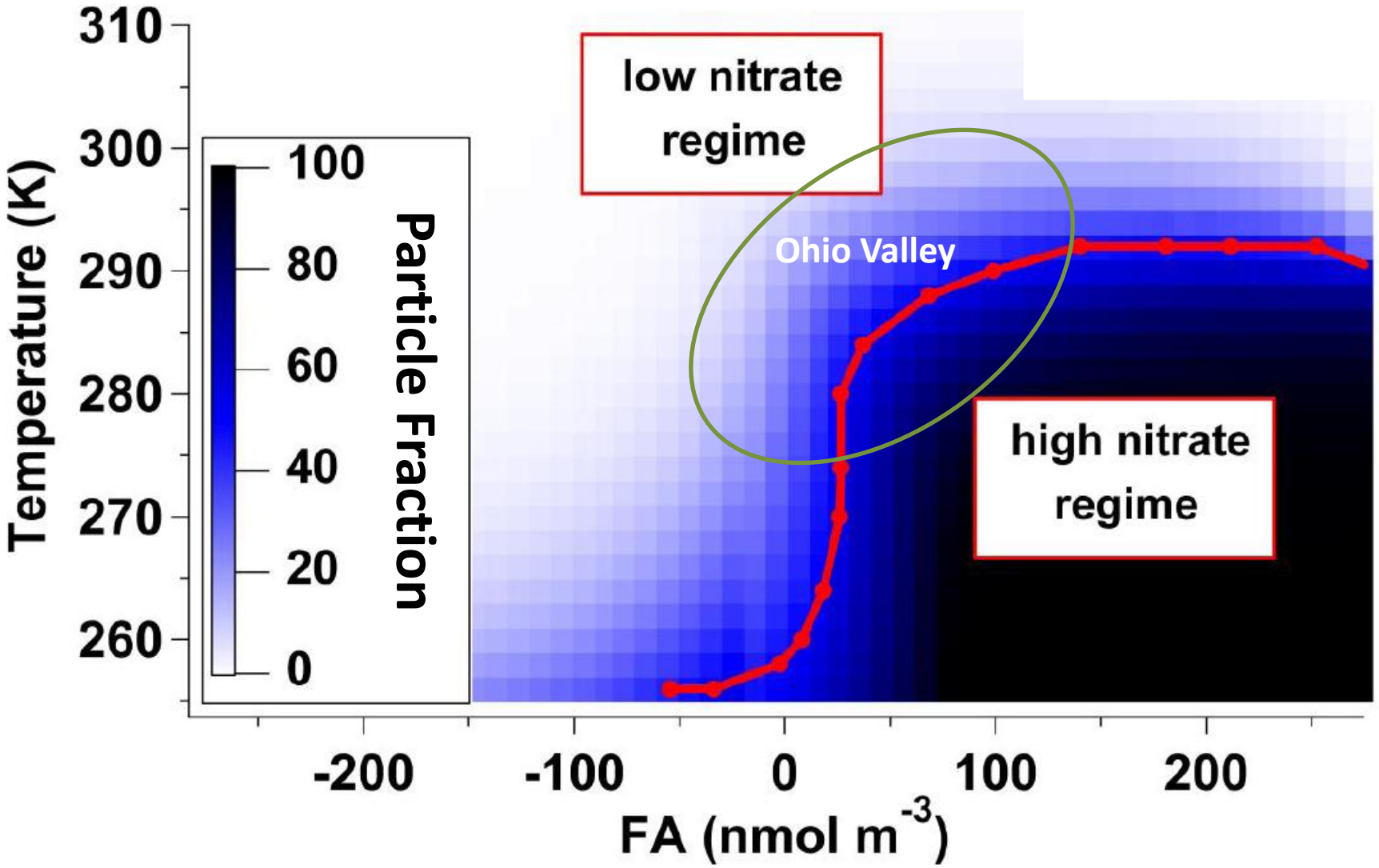


Figure 4-7. Seasonal variation of total ammonium (NH_3 + NH_4^+) concentration and NH_3/NH_4^+ ratio at Fresno during CRPAQS. Note that the y-axis on the right has a logarithm scale.

FREE AMMONIA, FA = TA – 2 * TS
= $[NH_4^+] + [NH_{3(g)}] - 2 * [SO_4^{2-}]$

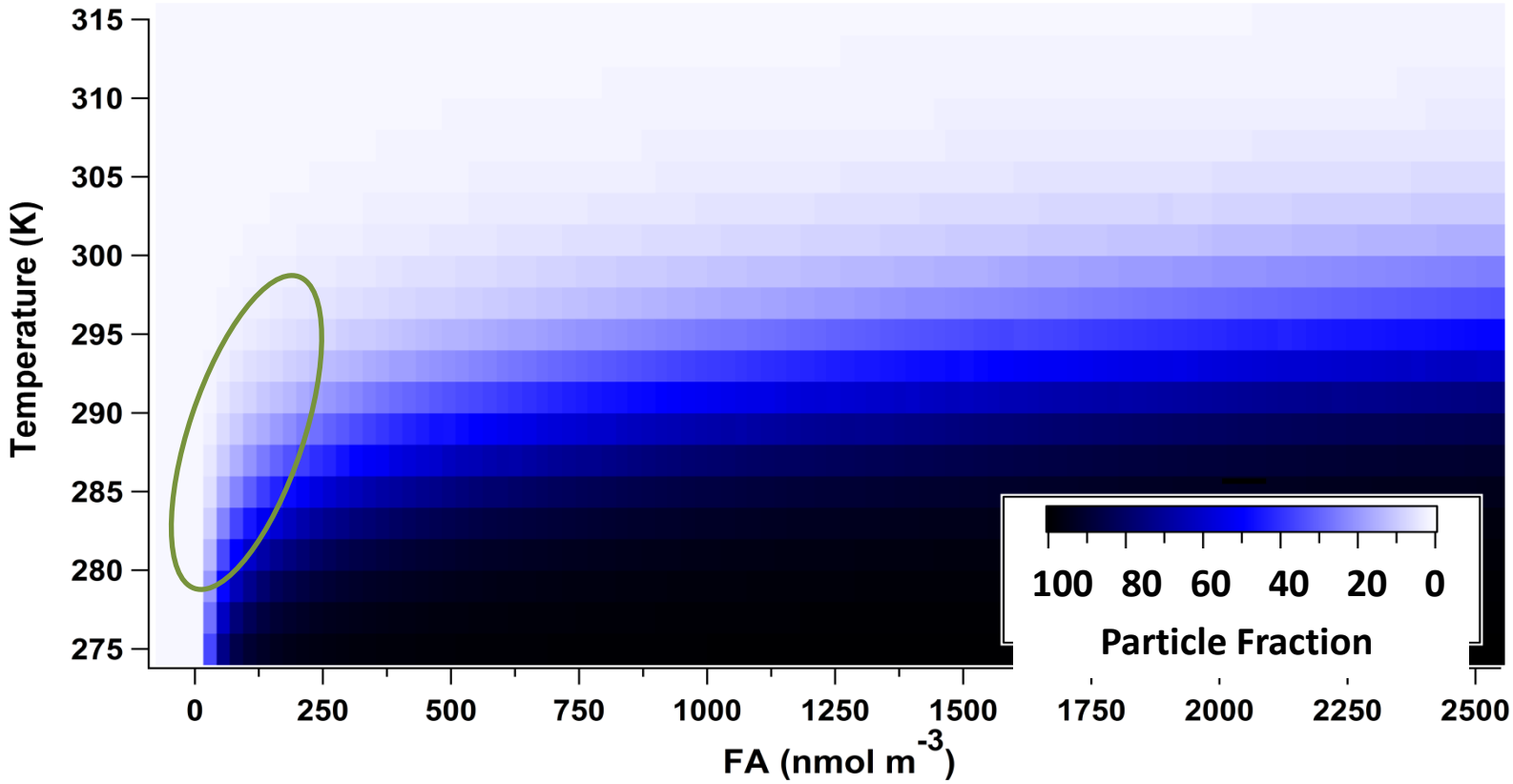


predict partitioning using ISORROPIA

Markovic *et al.,* Atmos. Chem. Phys., 2011

High NH_3, low TS and TN

Nitrate partitioning driven mainly by meteorology



Conditions:

RH = 40 %, T = 275 – 315 K, TN = 20 nmol m^{-3} , TS = 21 nmol m^{-3} , TA = 0 - 2750 nmol m^{-3}

FA values during the campaign = (-42 nmol m^{-3} to 2750 nmol m^{-3})

Pasadena data on chemical map generated assuming TN = 100 nmol m^{-3}
TN actually ranges from 10 – 700 and correlates with FA